Liquid-liquid equilibrium for the ternary system ethanol/toluene/n-decane: A correction to the existing coexistence curve and NRTL parameters

Tariq Allie-Ebrahim, Q. Zhu, G. D. Moggridge, C. D'Agostino*

Department of Chemical Engineering and Biotechnology, University of Cambridge, Pembroke Street, Cambridge, CB2 3RA, UK

*Corresponding Author:

Dr Carmine D'Agostino

Department of Chemical Engineering and Biotechnology

University of Cambridge

Pembroke Street

Cambridge

CB2 3RA, UK

Email: cd419@cam.ac.uk

Tel: +44(0)1223-761629

Abstract

A correction to the reported liquid-liquid equilibrium parameters using the non-random two liquid (NRTL) thermodynamic model for the ethanol/toluene/n-decane system at 298 K is reported. The parameters were calculated by minimising the residual between the calculated coexistence and the experimental compositions. However, to obtain a physically plausible coexistence curve, a parameter in the NRTL model had to be fixed. This highlights the importance of assessing the entire coexistence curve, as opposed to only comparing the calculated compositions to the experimental data points. This is because undertaking the regression for all the available parameters will result in a smaller residual and better fit of the calculated points to the experimental points. This leads to an apparent improved fit but the complete coexistence curve will show that the parameters are not physically plausible.

Keywords: *Thermodynamics, LLE, Ternary diagram, NRTL*

1. Introduction

The NRTL parameters presented by Mohsen-Nia [1] for ethanol/toluene/n-decane at 298 K produce a liquid-liquid equilibrium (LLE) coexistence curve that is entirely different from that which is experimentally reported in the same work. This paper identifies the causes of such inconsistency and provides a correction to these reported parameters. Before outlining the regression method used and the correct parameters, an overview of the thermodynamic requirements for two-phase liquid-liquid coexistence is presented.

2. Thermodynamic requirements

A system is only thermodynamically stable if the Gibbs energy, G, is a global minimum. This condition is both necessary and sufficient. Accordingly, the chemical potential energy of species i, μ_i, is constant across all phases [2]. This criterion is expressed in terms of the component activities, a_i, which are related to γ_i for liquids, between phase I and II:

$$a_i^I = x_i^I \gamma_i^I = x_i^{II} \gamma_i^{II} = a_i^{II} \quad (1)$$

Equation (1) is known as the iso-activity criterion. It is only a necessary equilibrium condition, as it could occur at a local minimum. The iso-activity criterion, in conjunction with a molar balance over the two phases, is preferred over minimising G to determine the LLE tie-lines, as it is less computationally expensive [3].

For VLE systems the iso-activity criterion is:

$$x_i \gamma_i P_i^{vap} = y_i P_{tot} \quad (2)$$

where P_i^{vap} is the vapour pressure of i and P_{tot} is the total vapour pressure. Equation (2) shows that for VLE systems it is possible to obtain an explicit value for γ_i, which is not the case for LLE systems as seen in Equation (1). This, coupled with the highly non-linear nature of the activity coefficient models due to multiple exponential terms, makes obtaining physically meaningful LLE parameters difficult.

An alternative to minimising the iso-activity criterion residual is to minimise the residual of the predicted tie-line compositions:

$$F_x = \sum_{i=1}^{3}\sum_{j=1}^{2}\sum_{k=1}^{M}\left(x_{ik}^{j} - \hat{x}_{ik}^{j}\right)^2 \quad (3)$$

where i is the component, j is the phase, k is the number of tie-lines (with M the total number of tie-lines) and x_{ik}^{j}, $\hat{x}_{ik}^{j}$ are the experimental and calculated mole fractions, respectively. However, solving for $\hat{x}_{ik}^{j}$ requires solving the iso-activity criterion at each tie-line, where Equation (1) is adjusted to make $\hat{x}_{ik}^{j}$ the subject of the equation. Equation (3) reflects the overarching objective of the LLE regression, that is, obtaining a good fit of the calculated and experimental compositions whilst ensuring thermodynamic consistency. The highly non-linear nature of this objective function results in multiple local minima. These local minima parameters are thermodynamically inconsistent. The difficult nature of the thermodynamic models often results in the degree to which the right-hand side and left-hand side of the iso-activity criterion differ being relaxed, or increased, in LLE regression. Since there are numerous compositions that are able to satisfy the iso-activity criterion with a small residual, inconsistent solutions are often obtained [4]. Thus, the iso-activity criterion must be enforced with an absolute residual of at most 10^{-4} to obtain a consistent solution.

The difficulty in LLE regression is compounded by the fact the NRTL model is able to correlate randomly generated LLE data, with similar objective function values as actual experimental data. Furthermore, the regressed ternary system parameters are typically unable to model the binary subsystems VLE using the NRTL model [3]. This highlights that even though there is a physical basis for the NRTL model, it remains empirical for LLE systems.

A recent comprehensive review published by Marcilla et al. [5] has indeed highlighted that many published parameters and LLE data contain serious inconsistencies, which were not detected due to the erroneous common conclusion on a good agreement between experimental and calculated tie-lines using these inconsistent parameters. The review identifies a series of possible causes for such inconsistencies and proposes a strategy to validate such parameters and ensure their consistency and quality.

3. Method and results

The NRTL parameters reported by Mohsen-Nia [1] produce a coexistence curve that is both inconsistent with the experimental data and vastly different from what is presented in the author's paper. The reported parameters erroneously predict that ethanol/toluene is partially miscible, as shown in Figure 1. Krishna [6] obtained the same erroneous coexistence curve when using these reported parameters. It is uncertain as to how these parameters were obtained, as no information or detail regarding the regression is provided.

Considering that Equation (1) is the dominant regression technique, it is expected and indeed found that many reported ternary parameters are thermodynamically inconsistent [4]. This is because, as discussed earlier, Equation (1) is only a necessary condition, which does not ensure that the solution is a global minimum. Furthermore, Equation (1) merely ensures thermodynamic consistency but it does not ensure that the calculated compositions compare well with the experimental data, as it is the case with Equation (3). In this work, the parameters for the ethanol/toluene/n-decane system are regressed using Equation (3). The tangent plane method [2] is used to confirm that the solution obtained is thermodynamically consistent.

Figure 1. Comparison of experimental LLE data for ethanol/toluene/n-decane at 298 K against the LLE obtained from the literature NRTL parameters provided by Mohsen-Nia [1] and complete regression of all the NRTL variables. Both sets of parameters yield inconsistent coexistence curves.

The ternary NRTL model has nine parameters, two interaction parameters for each binary system (τ_{ij}andτ_{ji}) and one non-randomness parameter for each binary system (ε_{ij}). Considering that there are only five experimental tie-lines available, there are only 15 constraints (three iso-activity relationships for each of the five tie-lines). Therefore the system is only weakly overdetermined, as there are only 15 equations for the 9 variables Thus, obtaining a physically consistent model is unlikely.

Indeed, regressing for all the parameters resulted in unphysical predictions, as seen in Figure 1, as the model incorrectly predicts that ethanol/toluene are only partially miscible, which is clearly not the case. An improved fit could be obtained by having more experimental data at intermediate $x_{\mathrm{n-decane}}$. This stresses the importance of

obtaining tie-lines close to the consulate point, as these data points have a large influence on the regression.

To overcome these unphysical conditions, certain model parameters must be fixed to physically meaningful values. As few variables as possible must be fixed, as this reduces the quality of the fit by reducing the degree of freedom of the regression.

The best NRTL solution that correctly predicts the complete miscibility of ethanol/toluene required ε_{12} to be fixed at 0.47, which the recommended value for a self-associating/non-polar binary systems [7].

The root-mean-square deviation, RMSD, for the regression is defined as:

$$RMSD = \left(\sum_{i=1}^{3} \sum_{j=1}^{2} \sum_{k=1}^{M} \frac{\left(x_{ik}^{j} - \hat{x}_{ik}^{j} \right)^2}{6M} \right)^{0.5} \quad (4)$$

The RMSD values for the regression analyses are provided in Table 1.

Table 1. RMSD for ethanol (1)/toluene (2)/n-decane (3) LLE regression at 298 K.

Figure 2. Experimental and regressed NRTL LLE coexistence region for ethanol/toluene/n-decane at 298 K. The experimental and calculated points overlap showing excellent consistency.

The physically consistent NRTL parameter values are provided in Table 2. The resultant coexistence curve is provided in Figure 2. The standard errors were determined by a local linear approximation of the variation in the sum of squares with the regression parameters. From Figure 2 it can be clearly seen as the predicted curve matches very well the experimental data reported for the system.

Table 2. Regressed NRTL parameters at 95% confidence level for ethanol (1)/toluene (2)/n-decane (3) at 298 K, with $\boldsymbol{\varepsilon_{12} = 0.47}$ using Equation (3).

4. Conclusions

The current parameters available in the literature for predicting LLE of ethanol/toluene/n-decane at 298 K give an incorrect coexistence curve, which leads to unphysical results. Furthermore, the resultant coexistence curve does not match the

reported experimental data. In this work, the correct NRTL parameters for the system are determined by minimising the difference between the calculated coexistence and the experimental compositions. These parameters are an improvement over those provided by Mohsen-Nia [1] and provide a physically plausible two-phase coexistence curve that agrees with the experimental data reported for the system. The determined parameters can therefore be used when performing thermodynamic modelling of this system.

Acknowledgements

Carmine D'Agostino is grateful to Wolfson College, Cambridge, for supporting his research activities.

Nomenclature

a_i	Activity of i	-
G	Gibbs energy	J.mol^{-1}.K^{-1}
M	Total tie-lines	-
P_{tot}	Total vapour pressure	bar
P_i^{vap}	Vapour pressure of i	bar
x_i	Mole fraction of i in the liquid	-
y_i	Mole fraction of i in the vapour	-
$\hat{x}_i$	Activity coefficient model calculated mole fraction of i	-

Greek Letters

ε_{ij}	NRTL non-randomness parameter between $i-j$	-
μ_i	Chemical potential energy of i	J.mol^{-1}.K^{-1}
γ_i	Activity coefficient of i	-
τ	NRTL $i-j$ interaction parameter	-

References

[1] Mohsen-Nia M, Ternary liquid–liquid equilibria for mixtures of (ethanol+toluene+n-decane). Physics and Chemistry of Liquids. 2007; 45: 541-8.
[2] Sorensen JM, Magnussen T, Rasmussen P, Fredenslund A, Liquid-liquid equilibrium data - Their retrieval, correlation and prediction. 2. Correlation. Fluid Phase Equilibria. 1979; 3 (1): 47-82.
[3] Li Z, Smith KH, Mumford KA, Wang Y, Stevens GW, Regression of NRTL parameters from ternary liquid-liquid equilibria using particle swarm optimization and discussions. Fluid Phase Equilibria. 2015; 398: 36-45.

[4] Marcilla-Gomis A, Reyes-Labarta J, Serrano-Cayuelas M, Olaya-Lopez M, GE models and algorithms for condensed phase equilibrium data regression in ternary systems: Limitations and proposals. Open Therm J. 2011; 5: 48-62.
[5] Marcilla A, Reyes-Labarta JA, Olaya MM, Should we trust all the published LLE correlation parameters in phase equilibria? Necessity of their assessment prior to publication. Fluid Phase Equilibria. 2016; http://dx.doi.org/10.1016/j.fluid.2016.11.009.
[6] Krishna R, Serpentine diffusion trajectories and the Ouzo effect in partially miscible ternary liquid mixtures. Phys Chem Chem Phys. 2015; 17 (41): 27428-36.
[7] Renon H, Prausnitz JM, Local compositions in thermodynamic excess functions for liquid mixtures. AiChE Journal. 1968; 14 (1): 135-44.